

# CELLULOSE AND CELLULOSE DERIVATIVES

HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS, AND  
TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

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## 438 XIV. Solutions

interference fringes. The displacement of these fringes (measured as the number of fringes) gives directly the difference in refractive-index between the two cells if the wavelength of the light and the thickness of the cells along the optic axis are known. A separate set of air-air fringes defines a reference position. The fractional number of fringes is easily obtained, but the difficulty of the interferometric method lies in the determination of the integer number of fringes (175). This difficulty can be overcome, but it seems that refractometry is an easier technique to apply in practice.

Many instruments for the measurement of refractive-index increments and procedures for their use have been described in the literature, and there are commercial instruments that operate on one or the other of the principles mentioned above. Manufacturers of refractometric instruments are Phoenix Precision Instrument Company, Inc., Philadelphia; Waters Associates, Inc., Framingham, Massachusetts; Polymer Consultants, Ltd., London, England; and Shimadzu Setskusho Ltd., Tokyo, Japan. Interferometric instruments are made by Hilger and Watts, Ltd., London, England; and Carl Zeiss, Oberkochen/Württemberg, Germany.

Extreme care in the preparation and handling of solutions must be exercised in order to obtain accurate values for  $\partial n/\partial c$ ; this matter is discussed by Norberg and Sundelöf (174). A sensitivity of the order of  $10^{-6}$  refractive-index units is often required in the measurements, and then absorption of water vapor and other gases must be taken into account. In mixed solvents where the components are organic liquids with low and differing vapor pressures, the refractive-index may change because of excessive evaporation of the more volatile component. As the polymer solute usually is present only in small amounts, this can introduce very large errors, especially if the refractive indices of the two liquids are very different. For such systems it is also necessary to have solution and solvent in dialysis equilibrium. In order to avoid evaporation errors a continuous-flow system is to be preferred, with solution and solvent flowing from the dialysis cell to the respective halves of the refractometer cell. For the complex cellulose solvents, high viscosity will cause other problems. The diffusion rate becomes low, and mixing takes place very slowly; this makes, for example, the cleaning of cells a slow and difficult undertaking. Striations are easily created, and it is necessary to wait sufficiently long to make sure that readings are stable and reproducible. The solvent FeTNa is particularly difficult to work with in this respect. These points have to be considered also in the light-scattering experiments.

Some refractive-index increments for cellulose and cellulose derivatives under different conditions of solvent and wavelength are listed in Table 2.

TABLE 2  
Refractive-Index Increments of Solutions of Cellulose and Cellulose Derivatives.

Polymer	Solvent	$T(^{\circ}\text{C})$	$\lambda = 436 \text{ nm}$	$\lambda = 546 \text{ nm}$	Remarks <sup>b</sup>	Ref.
Cellulose	Cadoxen (diluted 1 : 1 with water)	25	0.186 D	0.183 D		102
	Cadoxen (diluted 1 : 1 with water; no NaOH)	25	0.1927 D	0.1890 D		117
	Cuoxam (0.205 M Cu)	20	0.1317	0.1295	from diffusion measurements	176
	Cuen (0.0518 M Cu)	25	0.2574 D	0.117	Calculated from Lorenz-Lorentz formula	176
	Cuen (0.0776 M Cu)	25	0.1352			117
		25	0.2653 D			117
	FeTNa	25	0.344 D	0.178		120
Cellulose acetate	Acetone	-	-	0.104-0.116		177
Cellulose trifluoroacetate	Chloroform (+ 1 vol % absolute ethanol)	25	0.0406 ( $\lambda$ unspecified)			178
	Chloroform (+ 1 vol % absolute ethanol)	55	0.0496 ( $\lambda$ unspecified)			178
Cellulose tributylate	Methyl ethyl ketone	?	0.0926	0.0910		179
	Tributyltin	?	0.0368	0.0347		179

<sup>a</sup> The letter "D" indicates that measurements were performed on dilute solutions.

<sup>b</sup> Degree of substitution, or equivalent. If not listed here, see Table 3.

Polymer	Solvent	$T(^{\circ}\text{C})$	$\Delta n/\Delta c$ (ml/g) <sup>a</sup>	$\lambda = 436 \text{ nm}$	$\lambda = 546 \text{ nm}$	Remarks <sup>b</sup>	Rct.
441	Sodium carboxymethyl-cellulose	25	0.144 D	0.142 D	0.142 D	DS = 1.06	107
	Cadoxen (diluted 1 : 1 with water)	25	0.1896 D	0.1373 D	0.1861 D	DS = 0.96	117
	Cadoxen (diluted 1 : 1 with water; no NaOH)	25	0.1398	0.134 D	0.1373 D	DS = 1.06	107
	0.2 M NaCl	25	0.142	0.138 D	0.140	DS = 1.06	107
	0.005 M NaCl	25	0.146	0.136 D	0.144		110
	0.5 M NaCl	?	0.154				110
	Ionic strength lower than 0.5 M NaCl	?	0.158			Calculated from Gladstone-Dale data	114
	Methanol	25	0.130				184
	Water	20	-		0.146	Average value	161
	(Ethyl)(hydroxyethyl)-cellulose	?	-		0.148		162
441	Hydroxyethylcellulose	25	0.141	0.133	0.131	$\Delta n/\Delta c$ decreases 2% when temperature is raised from 3 to 58°C	114
	Water	25	0.139				160
	0.5 M NaCl	25	0.132				114
	Cadoxen (diluted 1 : 1 with water)	25	0.1504 D	0.1478 D	0.1247		117
	Cadoxen (diluted 1 : 1 with water; no NaOH)	25	0.1631 D				117
	Cuen (0.0518 M Cu)	25	0.1314				117

TABLE 2 (Continued)

Polymer	Solvent	$T(^{\circ}\text{C})$	$\Delta n/\Delta c$ (ml/g) <sup>a</sup>	$\lambda = 436 \text{ nm}$	$\lambda = 546 \text{ nm}$	Remarks <sup>b</sup>	Rct.
440	Cellulose triacetate	7	0.2069	0.2176	0.2033		181
	Acetone	27	0.2155	0.2176	0.2033		182
	Acetone	25	0.1556	0.1666	0.1666		182
	Cyclohexanone	25	-	0.210	0.210		183
	Dibutyl ketone	25	0.1911	0.1797	0.1797		182
	Diethyl ketone	25	0.1651	0.1558	0.1558		182
	Dioxane	20	0.168	0.156	0.156		112
	Dioxane	25	0.173 D	0.170 D	0.170 D	DS = 0.21	83
	Cadoxen (diluted 1 : 1 with water)	25	0.163 D	0.162 D	0.162 D	DS = 0.44	83
	Cadoxen (diluted 1 : 1 with water)	25	0.148 D	0.145 D	0.145 D	DS = 0.94	83
440	Cellulose triacetate	24	0.0442	0.0478	0.0478		180
	1-Chloronaphthalene	41	-	0.147	0.147		180
	Dimethylformamide	63	-	0.104	0.104		180
	Dioxane-water (100 : 7 by volume)						
	Cellulose triacetate	7	0.2069	0.2176	0.2033		181
	Acetone	27	0.2155	0.2176	0.2033		182
	Acetone	25	0.1556	0.1666	0.1666		182
	Cyclohexanone	25	-	0.210	0.210		183
	Dibutyl ketone	25	0.1911	0.1797	0.1797		182
	Diethyl ketone	25	0.1651	0.1558	0.1558		182
440	Sodium carboxymethyl-cellulose	25	0.173 D	0.170 D	0.170 D	DS = 0.21	83
	Cadoxen (diluted 1 : 1 with water)	25	0.163 D	0.162 D	0.162 D	DS = 0.44	83
	Cadoxen (diluted 1 : 1 with water)	25	0.148 D	0.145 D	0.145 D	DS = 0.94	83
	Cellulose triacetate	7	0.2069	0.2176	0.2033		181
	Acetone	27	0.2155	0.2176	0.2033		182
	Acetone	25	0.1556	0.1666	0.1666		182
	Cyclohexanone	25	-	0.210	0.210		183
	Dibutyl ketone	25	0.1911	0.1797	0.1797		182
	Diethyl ketone	25	0.1651	0.1558	0.1558		182
	Dioxane	20	0.168	0.156	0.156		112

TABLE 2 (Continued)

## 3. Other Applications of Light Scattering

The more important light-scattering investigations on solutions of cellulose and cellulose derivatives are listed in Table 3 for quick reference. In general a fairly true picture of the properties of molecules of cellulose and cellulose derivatives has been obtained; this is discussed in Section G of this Chapter XIV.

There are, however, points that are less clear, perhaps the behavior of the second virial coefficient is the most obvious of these. A very irregular correlation of the second virial coefficient with molecular weight has been found sometimes for solutions of (ethylhydroxyethyl)cellulose (162), cellulose nitrate (172), and cellulose tricarbanilate (182). Poorer agreement between values obtained from light scattering and osmosis has also been observed (182, 203). This makes uncertain (204, 205) an analysis of the data in terms of current theories. These effects could be due to the influence of molecular-weight distribution and with specific interactions in solution.

Without aiming at completeness it is of interest to mention briefly some other applications of light-scattering to cellulose systems.

TABLE 3

Summary of More Important Light-Scattering Investigations on Cellulose and Cellulose Derivatives in Solution

Each brief summary gives range of molecular weight; polymolecularity ratio; degree of substitution (DS) or equivalent; temperature; angular range; and symbols indicating wavelength of light used ( $V = 436$  nm,  $G = 546$  nm) and whether studies were made of depolarization ( $D$ ), refractive-index increment ( $R$ ), molecular dimensions ( $S$ ), or second virial coefficient ( $A$ ). If ultracentrifugation was used, this is indicated by the term "DK-cells." Other relevant comments of importance are given, followed by the literature citation.

## Cellulose

In cadexen.  $(M)_w$ : 215,000-945,000;  $(M)_w/(M)_n \approx 2$  (for one fraction 7.7); 25°C;  $V + G$ ,  $R$ ,  $S, A$ ; DK-cells; thorough discussion of dialysis (103).

In cadexen.  $(M)_w$ : 16,500-33,800;  $(M)_w/(M)_n$ : 1.7-2.2; 25°C;  $V + G$ ,  $D$ ,  $R$ ,  $A$ ; DK-cells (191).

In FeNa.  $(M)_w$ : 63,000-640,000; 25°C (?);  $D$ : 30-150°;  $G, R, S, A$ ; dialysis discussed; light absorption corrected for (120).

## Cellulose Acetate

In acetone.  $(M)_w$ : 52,000-163,000; solution thermostated, no temperature given;  $D$ : 51-129°;  $G, D, R, S, A$  (177).

In chloroform (1 vol % absolute alcohol to prevent decomposition).  $(M)_w = 156,000$ ; 61.5% acetic acid yield; 21-56°C;  $D$ : 40-130°;  $\lambda$  not given,  $D, R, A$ ; formation of aggregates studied (178).

\*  $DS_{2,3}$  and  $DS_4$  denote degrees of substitution at  $C_2$  and  $C_3$ , and at  $C_4$ .  
\*  $(\partial n/\partial c)$  in milliliters per gram of cellulose.

Ref.	Remarks <sup>b</sup>	$\lambda = 436$ nm $\lambda = 546$ nm	$\partial n/\partial c$ (ml/g) <sup>a</sup>	Temperature T (°C)	Solvent	Polymer
185	No change after irradiation and branching	0.145	?	?	Water	Methylcellulose
186						
168	13.4% N (cf. Fig. 7)		0.154	24(?)	Water	Cellulose nitrate
171	13.9% N (cf. Fig. 7)		0.107	?	Acetone	
187	13.7-14.1% N		0.0930	25	Acetone	
187	13.9% N		0.105	25	Acetone	
172	12.9% N		0.1116	25	Acetone	
172	13.57-13.80% N		0.1151	25	Acetone	
172	13.57-13.80% N		0.105	25	Acetone	
188	13.49-13.54% N		0.104	25	Acetone	
189	11.3-13.8% N		0.102	30	Ethyl acetate	
141	$A$ and $B$ are values for two different solvent preparations	0.144 ( $A$ ) 0.079-0.098 ( $B$ )	24±1		Dimethyl sulfoxide-water (9:1 by weight)	Diethylacetamide
190		0.082			Dimethyl sulfoxide	cellulose xanthate
108			0.080	?	1 M NaOH	Sodium cellulose xanthate <sup>c,d</sup>
			$(\frac{\partial n}{\partial c})_{546} = 0.186 + 0.25 \cdot DS_{2,3} + 0.15 \cdot DS_4$ $(\frac{\partial n}{\partial c})_{546} = 0.183 + 0.22 \cdot DS_{2,3} + 0.13 \cdot DS_4$	5		

TABLE 3 (Continued)

## Cellulose Tributylate

In methyl ethyl ketone.  $\langle M \rangle_w$ : 62,000–313,000; temperature not given;  $\theta$ : 45–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (179).

## Cellulose Tricaproate

In dimethylformamide (41°C,  $\theta$ -conditions), 1-chloronaphthalene (24°C), dioxane–water (100 : 7 by volume, 63°C).  $\langle M \rangle_w$ : 41,700–1,480,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 1.03–1.76;  $\theta$ : 45–125°;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (180).

## Cellulose Tricarbanilate

In acetone.  $\langle M \rangle_w$ : 67,200–2,665,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 1.1–1.8; 8.19–8.36%  $N$ ; 7 and 27°C;  $V + G$ ,  $R$ ,  $S$ ,  $A$  (181, 192).

In various mixtures: dioxane–methanol ( $\theta$ -conditions: 57.5 vol % MeOH); acetone–water ( $\theta$ -conditions: 7.8 vol % water); methyl ethyl ketone–methanol ( $\theta$ -conditions: 57 vol % MeOH); dipropyl ketone–methanol ( $\theta$ -conditions: 52 vol % MeOH);  $\langle M \rangle_w$ : 840,000; 8.33%  $N$ ; 20°C;  $\theta$ : 30–150°;  $\lambda$ : 3610, 4360, 5460 Å;  $S$ ,  $A$  (111).

In dioxane and dioxane–methanol (44:56 by volume).  $\langle M \rangle_w$ : 370–6950; 20°C;  $\lambda$ : 3610, 4360, 5460 Å;  $R$ ,  $S$ ,  $A$  (112).

In anisole ( $\theta$ -conditions at 94°C) and cyclohexanol ( $\theta$ -conditions at 73°C).  $\langle M \rangle_w$ : 430,000–2,170,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 2; 8.04–8.07%  $N$ ; 94°C (90–123°C) for anisole, 73°C (71–86°C) for cyclohexanol;  $G$ ,  $S$ ,  $A$ : DK-cells (193).

In acetone, cyclohexanone, diethyl ketone, dioxane.  $\langle M \rangle_w$ : 315,000–2,170,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 2; 8.04–8.07%  $N$ ; 25°C;  $\theta$ : 35–135°;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (182).

In diethyl ketone.  $\langle M \rangle_w$ : 2,300,000 (association: in original sample  $\langle M \rangle_w$  = 315,000;  $\approx$  2; 8.04–8.07%  $N$ ; 25°C;  $\theta$ : 35–135°;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (182)).  $\langle M \rangle_w/\langle M \rangle_n$  = 1.85 (original sample); 8.04%  $N$ ; 6–47°C;  $\theta$ : 15–135°;  $G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells; apparent second virial coefficient is zero at both 10 and 42°C and passes through a maximum at approximately 27°C; the radius of gyration also has a maximum at approximately 27°C (183).

## Sodium Carboxymethylcellulose

In water, 0.001–0.05  $M$  NaCl, and various isotonic mixtures (NaCl).  $\langle M \rangle_w$ : 36,000; 25°C;  $\theta$ : 30–135°;  $V$ ,  $S$ ,  $A$ : polyelectrolyte properties discussed (109).

In 0.005–0.5  $M$  NaCl.  $\langle M \rangle_w$ : 440,000;  $\langle M \rangle_n$ : 165,000; DS = 1.15; temperature not given;  $\theta$ : 30–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : polyelectrolyte properties discussed (110).

In 6% NaOH (190).  $\langle M \rangle_w$ : 49,000–1,055,000; DS: 0.21–0.96; 25°C;  $\theta$ : 45–135°;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells; dialysis performed (83).

In 0.005–0.2  $M$  NaCl and cadoxen.  $\langle M \rangle_w$ : 147,000–1,060,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 2.1–4.3; DS: 1.06; 25°C;  $\theta$ : 45–135°;  $V + G$ ,  $D$ ,  $R$ ,  $S$ ,  $A$ : DK-cells; dialysis discussed (107).

TABLE 3 (Continued)

## Ethylcellulose

In methanol.  $\langle M \rangle_w$ : 98,000–410,000; 25±1°C;  $\theta$ : 32–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : second virial coefficient approximately zero for all fractions (184).

## (Ethyl)hydroxyethylcellulose

In water.  $\langle M \rangle_w$ : 160,000–570,000; DS = 0.84 with respect to ethoxyl and DS = 0.56 with respect to ethylene oxide (average values); room temperature (31); 40–135°;  $V + G$ ,  $D$ ,  $R$ ,  $S$ ,  $A$ : difficulties with gel particles are discussed (162).

## Hydroxyethylcellulose

In water.  $\langle M \rangle_w$ : 190,000–625,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 1.52–1.81; molar substitution: 1.57–1.64; 25°C;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (160).

In water, endoxen. 0.5  $M$  NaCl, 0.5  $M$  HCl, and 0.5  $M$  NaOH.  $\langle M \rangle_w$ : 80,000–625,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 1.52–1.65; molar substitution: 1.57–1.68; 3–58°C (25°C for most fractions);  $\theta$ : 45–135°;  $V + G$ ,  $R$ ,  $S$ ,  $A$ : DK-cells; dialysis performed (114, 194).

In water–dimethyl sulfoxide (0–100 vol % DMSO) and water–formamide (0–80 vol % formamide).  $\langle M \rangle_w$ : 465,000 (original sample); molar substitution: 1.67; 25°C;  $V$ ,  $R$ ,  $S$ ,  $A$ : DK-cells; anomalous results due to solvent effects and association; variation in solvent power with composition (66).

## Methylcellulose

In water and 0.5  $M$  NaCl (contains also measurements on hydroxypropyl derivatives of methylcellulose).  $\langle M \rangle_w$ : 122,000–570,000 (298,000–690,000 for hydroxypropyl derivative); 28.0–31.1% methoxyl (21.6–28.1% methoxyl and 11.4–3.72% hydroxypropyl); 24°C (7);  $\theta$ : 30–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : solution treatment and aggregation discussed (186).

## Cellulose Nitrate

In acetone.  $\langle M \rangle_w$ : 9,400–518,000; 13.18–13.96%  $N$ ;  $\sim$  25°C;  $\theta$ : 53–124°;  $G$ ,  $D$ ,  $R$ ,  $S$ ,  $A$  (170).

In acetone.  $\langle M \rangle_w$ : 77,000–2,640,000; 13.7–14.1%  $N$ ; 25±1°C;  $\theta$ : 30–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : polymolecularity is discussed in the first paper (95, 171).

In ethyl acetate.  $\langle M \rangle_w$ : 41,300–573,000;  $\langle M \rangle_w/\langle M \rangle_n$ : 1.19–2.23; 13.49–13.54%  $N$ ;  $\sim$  25°C;  $\theta$ : 30–135°;  $V$ ,  $D$ ,  $R$ ,  $S$ ,  $A$ : discussion of polydispersity corrections (188).

In ethanol.  $\langle M \rangle_w$ : 20,000–200,000; 12.2–12.6%  $N$ ; 3–39.3°C;  $\theta$ : 45–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : many aspects of aggregation and the dependence on the pretreatment of solutions is discussed (163).

In acetone and ethyl acetate.  $\langle M \rangle_w$ : 650,000–2,500,000; 13.57–13.80%  $N$ ; 25°C;  $\theta$ : 30–135°;  $V$ ,  $R$ ,  $S$ ,  $A$ : DK-cells (172).

In acetone.  $\langle M \rangle_w$ : 2,580,000–2,880,000; 13.75%  $N$ ; temperature not given;  $\theta$ : 35–135°;  $G$ ,  $S$ ,  $A$ : DK-cells (modified) (157).

## XVII. Derivatives of Cellulose

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## C. ETHERS

A. B. Savage

The purpose of this chapter is not to repeat information already given in Chapter IX-E of Part II, but to supplement it with information developed since the mid-1950s.

During the last decade the cellulose ethers have progressed from materials of largely experimental and developmental importance to products of considerable industrial importance. The most important products are shown in Table I.

The production of sodium carboxymethylcellulose has steadily increased both in the United States and abroad. Its utility has changed from essentially 90% for drilling muds in the oil industry to a variety of uses, including food additives, paper sizes, and antiredeposition agents in detergents. The production of methylcellulose has also increased. The introduction of (hydroxypropyl)-(methylcellulose) has greatly broadened the use field of the methylcelluloses. The production of water-soluble hydroxyethylcellulose has approached that of the older water-soluble ethers. Low-degree-of-substitution hydroxyethylcellulose films are being produced (see Section E of Chapter XIX).

The various water-soluble ethers have generally similar properties, but there is only a partial direct competition among them. For example, sodium carboxymethylcellulose and hydroxyethylcellulose do not generally gel from their solutions on being heated. On the other hand, the materials of the methylcellulose group have distinct gelation temperatures. In general the nongelling derivatives will be more useful where high temperatures of use are encountered, but the methylcellulose group will be more useful in applications in which gelation is a distinct advantage.

The only organosoluble ethers produced commercially are ethylcellulose, which has been produced at a constant rate over the last two decades, and cyanoethylcellulose, which is used in small quantities in the manufacture of electroluminescent articles because of its high dielectric constant (see section D of this Chapter XVII).

The primary improvements that have been made during the last decade are in the physical form (e.g., granular) of the ethers and the growing use of surface crosslinking to facilitate dispersion. With the aid of dialdehydes, such as glyoxal,

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TABLE I  
Types of Commercial Cellulose Ethers (1)

Cellulose ether	Reagent	Range of utility	
		Solubility	DS
Sodium carboxymethylcellulose	Chloroacetic acid or sodium salt	Water	0.5-1.2
Methylcellulose (Hydroxypropyl)(methyl)cellulose	Methyl chloride	Water	1.5-2.4
	Methyl chloride and propylene oxide	Water	1.5-2.0
(Hydroxyethyl)(methyl)cellulose	Methyl chloride and ethylene oxide	Water	1.5-2.0
Hydroxyethylcellulose Ethylcellulose	Ethylene oxide	Water	1.3-3.0 <sup>a</sup>
	Ethyl chloride	Organic solvents	2.3-2.6
(Ethyl)(hydroxyethyl)cellulose	Ethyl chloride and ethylene oxide	Water	1.4-1.6
(Ethyl)(methyl)cellulose	Ethyl chloride and methyl chloride	Water	1.0-1.3
Sodium (carboxymethyl)-(hydroxyethyl)cellulose Cymethylocellulose	Chloroacetic acid and ethylene oxide	Water	0.3 <sup>b</sup> , 0.7 <sup>c</sup>
	Acrylonitrile	Organic solvents	0.4 <sup>b</sup> , 0.3 <sup>c</sup>

<sup>a</sup> Given in terms of molar substitution.<sup>b</sup> Substitution value for carboxymethylcellulose.<sup>c</sup> Substitution value for hydroxyethylcellulose.

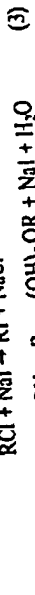
products that can be slurried to wet them out without development of viscosity can be prepared, and viscosity will develop rapidly as soon as the pH of the solution is changed.

The trend in alkali cellulose preparation is toward continuous or toward *in situ* preparation by spraying and mixing, or slurrying and pressing (e.g., in a screw press), or by slurrying in an organic liquid. Attention is being directed to the use of wood pulp instead of cotton linters. Although sodium hydroxide is used almost universally in the production of soluble cellulose ethers, it has been shown that in treating small amounts of textiles other bases (such as cesium or rubidium hydroxides) produce a more rapid initial reaction; however, after 30 min of reaction, the rate obtained by using sodium hydroxide appeared to be equally fast (2).

Additional highlights of new information on cellulose ethers, including some corrections to the previously published volumes, are discussed below.

Sodium chloromethanesulfonate has been found to react with alkali cellulose, provided water is removed to drive the reaction to completion: this is not necessary in the case of sodium  $\beta$ -chloroethanesulfonate (3).

Although only the alkyl chlorides are used to make soluble alkyl cellulose ethers commercially, cloth has been treated with relatively nonreactive reagents and reasonable substitutions have been obtained by introducing iodide salts to serve as intermediates (4). The iodide salts react with relatively inactive organic chlorides or bromides to give the corresponding organic iodides. The iodides react more readily with cellulose, and the iodide salts are then re-formed:



Advances that have been made in the study of the rates of reaction of organic compounds have been applied to cellulose: the general discussion of reaction mechanisms by Ingold (5) is excellent in this respect. In general alkali cellulose attacks alkyl halides by  $S_N2$  nucleophilic bimolecular mechanisms. If the substituent is large, solvent effects enter in, and the organic liquid used must be suited to the particular reaction. Thus methyl or ethyl chloride reacts by the  $S_N2$  mechanism, but chloroacetic acid approaches an  $S_N1$  mechanism. One may ethylate in ethyl chloride or benzene, but one would prefer isopropyl alcohol or *t*-butyl alcohol as a liquid in carboxymethylation. Postulated mechanisms for ethylation and its side reactions have been verified with the aid of an analog computer (1).

In a note of correction to Part II, page 898, the preparation of 2-methylcellulose was claimed by Sugihara and Wolfrom. They obtained indications of this from a 12% overall yield (6). In another correction, although ethylenimine was said to serve as its own catalyst in reacting with cellulose (in Part II, p. 958), reality acid catalysis is required. Early German ethylenimine preparations contained sulfuric acid residues that served to catalyze the reaction.

Ethers derived from  $\alpha, \beta$ -unsaturated compounds, especially acrylonitrile, have been the object of much research during the last decade: they are described in Section D of this Chapter XVII. Crosslinked ethers are covered in Section E of this Chapter XVII. Information on some recent developments in the uses of cellulose ethers may be found in Chapter XIX, especially in Sections A, B, D, E, H, and I.

### 1. Sodium Carboxymethylcellulose

The development of organic-liquid-slurry techniques, in a process and plant that might be used interchangeably to make several ethers, was an important advance. It made possible *in situ* preparation of alkali cellulose, attainment of